

Local Mode Transferability from Cubic Perovskite to Hexagonal Barium Titanate

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Abstract. We have performed a first-principles study of the zone-center optical modes of hexagonal BaTiO₃, showing that all the experimentally relevant low-energy modes are characterized by the same local polar distortions that determine the ferroelectric instability of the cubic perovskite. The influence of the particular stacking of the TiO₆ groups in the hexagonal structure and the occurrence of previously unreported low-energy Rigid Unit Modes are addressed.

I INTRODUCTION

Barium titanate has two structural polymorphs: the cubic perovskite type (c-BT) and its hexagonal modification (h-BT) with thirty atoms per unit cell. While c-BT has been one of the best studied ferroelectric materials for decades [1], work on the structural and dielectric properties of h-BT is scarce, most of it in the past decade [2]. It seems to be well established that h-BT undergoes two zone-center structural phase transitions: at 222 K from the high temperature $P6_3/mmc$ hexagonal phase to a second non-polar $C222_1$ phase, and at 74 K to a ferroelectric $P2_1$ phase. The first transition is associated with the softening of an optical mode and the second attributed to a shear strain instability, but the microscopic origin of the instabilities has not been determined yet mainly due to the absence of structural information on the two low-symmetry phases.

On the other hand, the discovery of a giant LO-TO splitting in h-BT by Inoue *et al.* [3] suggested that its ferroelectric modes have the same origin as those of c-BT. In c-BT, the soft [4] distortions can be essentially described as chains of dipoles that

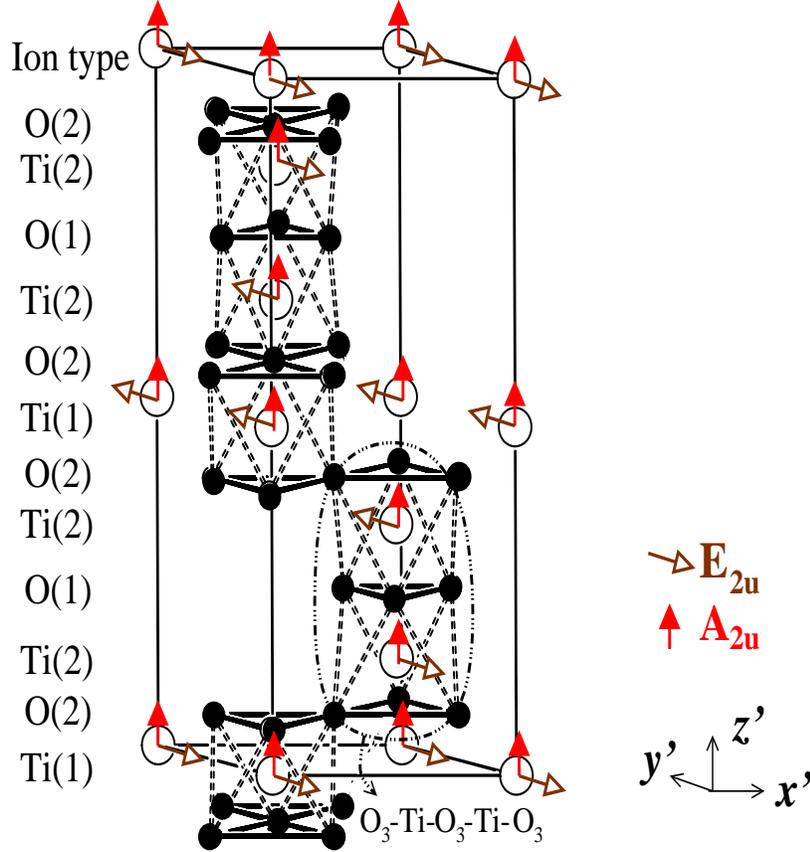


FIGURE 1. Structure of the hexagonal phase of h-BT, where the different kinds of ions are indicated (Ba ions are not shown for simplicity). The arrows along z' (resp. in the $x'y'$ plane) stand for the distribution of Ti displacements leading to the A_{2u} soft mode (resp. E_{2u} instability). In the case of E_{2u} , the Ti ions can move in any direction of the $x'y'$ plane, and the important thing to notice is the correlation (in-phase or anti-phase) of the movements of the different Ti ions.

originate in the movement of Ti ions relative to their surrounding O_6 octahedra with a minor distortion of the latter. As shown in Fig. 1, h-BT is also composed of TiO_6 groups that, despite a complicated arrangement, which markedly differs from that of the perovskite, can lead to chains of dipoles if properly distorted. Note, for instance, that the displacement of Ti ions along z' would produce chains whose elementary constituent can be depicted as $O_3-Ti \Rightarrow O_3$ (the Ti ion approaches one O_3 face of the octahedron), which, from a local point of view, is the distortion corresponding to the rhombohedral phase of c-BT. Then, the question is: To what extent can the instabilities of c-BT be transferred to h-BT and help us to understand its behaviour? Obviously, if this transference can be actually done, it would have implications for other materials composed of TiO_6 (or similar) groups.

In the following, we summarize our first-principles [5] study of h-BT, addressing

Irrep	experimentally reported		other soft modes			E_{1u}^f
	E_{2u}	A_{2u}^f	A_{2g}	B_{1u}	B_{2g}	
Ab-initio cell	-0.0123	0.0074	0.0061	0.0093	0.0098	0.3305
Exp. cell	-0.0284	-0.0256	0.0059	0.0080	0.0100	0.3083

TABLE 1. Force constants (in a.u.) of the low-energy zone-center normal modes of the $P6_3/mmc$ phase of h-BT. The last column shows the high-energy E_{1u} mode that is dominated by the Ti movement (forming chains of dipoles). The ferroelectric modes are marked with a superindex f .

the issues of the microscopic origin of all the low-energy modes of the structure, and of the influence of the stacking of the TiO_6 octahedra. In the spirit of the approach used for the construction of local modes and effective hamiltonians from *ab initio* calculations [6], the experimentally found zone-center soft modes are analyzed in terms of the distortion of the TiO_6 groups, and the results are compared to those of the c-BT.

II EXPERIMENTALLY FOUND SOFT MODES

In h-BT, the experimentally found optical soft modes are: the zone-center instability that drives the phase transition at 222 K and transforms according to the E_{2u} irreducible representation (irrep) of $6/mmm$, and the A_{2u} ferroelectric mode that softens (without becoming unstable) in the temperature range of the $C222_1$ phase and is responsible for the experimentally found giant LO-TO splitting. Our calculations of the phonon [7] spectrum at Γ agree with this experimental evidence. We considered two different unit cells: the experimentally determined one (with $a = 10.77$ and 26.451 a.u. [8]) and the ab-initio relaxed one (with 10.68 and 26.053 a.u.). In both cases, we get an unstable E_{2u} mode whose force-constant is shown in Table 1. [As usual, the instability is stronger in the bigger cell.] With respect to A_{2u} , we obtain an unstable mode for the experimental unit cell, while the same mode (the eigenvectors are essentially identical) is stable (but still soft) in the *ab initio* cell. [The occurrence of this second instability in our calculations does not contradict the experimental evidence, since the A_{2u} modes are symmetrical in the low-temperature phase of the crystal. Incidentally, from the point of view of symmetry, this A_{2u} soft mode could drive the transition at 74 K.]

In order to study the microscopic origin of the soft modes, attention must be paid to the corresponding eigenvectors. In both cases, the Ba contribution is small (around 10% of the total mode vs. 4% in the perovskite). Moreover, we checked that if the Ba ions are frozen at their high-symmetry positions the modes are still soft, so we do not consider Ba in the following discussion. For the analysis of the displacements of the Ti and O ions, which we want to compare to the instabilities of the perovskite, we focus on the distortions of the TiO_6 groups. There are two kinds of octahedra in h-BT: those centered round $\text{Ti}(1)$ ions at $2a$ Wyckoff position with

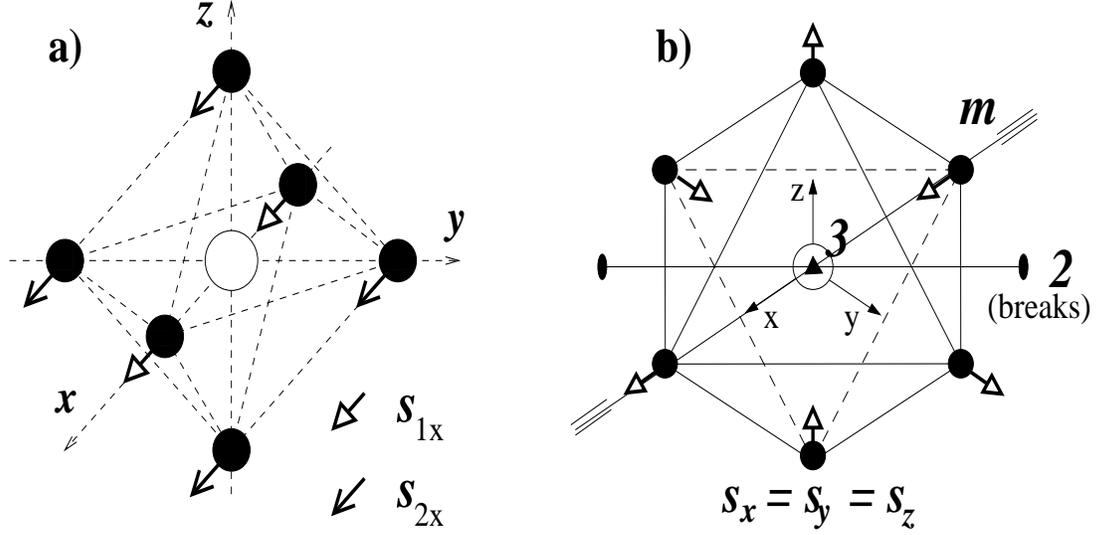


FIGURE 2. Panel a): Symmetry adapted displacement patterns defining the structure of the local modes that describe the zone-center instability of c-BT (cartesian coordinates are used). Only the modes along x are shown, but the same applies to y and z coordinates. Panel b): TiO_6 group projected along $(x, y, z) = (1, 1, 1)$ (along z' in the hexagonal basis of Fig. 1), and distorted with a local mode of the form $s_{ix} = s_{iy} = s_{iz}$ (only $i = 1$ is shown; the same applies to $i = 2$). Assuming that the undistorted octahedra has the indicated $\bar{3}m$ point symmetry (that of $\text{TiO}_6(1)$ taking the origin in the Ti ion), it can be easily seen that the depicted distortion only retains $3m$.

$\bar{3}m$ point symmetry (denoted by $\text{TiO}_6(1)$) and those arranged around Ti(2) ions at $4f$ Wyckoff position with $3m$ point symmetry ($\text{TiO}_6(2)$). From group-theoretical considerations, it can be proven that the displacement of Ti(1) or Ti(2) ions along z' (i.e., any z' -like polar distortion of the octahedra) produces zone-center modes transforming with A_{2u} irrep, and that the movement in the $x'y'$ plane ($x'y'$ -like polar distortions of the octahedra) produces zone-center E_{2u} modes, provided in both cases that the displacements are correlated as depicted in Fig. 1. This means that, in principle, the soft modes of the hexagonal structure can originate in local polar distortions of the TiO_6 groups, i.e., in the occurrence of local dipoles that form chains and give rise to destabilizing Coulomb forces, as it happens in the perovskite.

Since the surrounding of the octahedra markedly differs between the two structures, we take the Ti location as the origin of coordinates and focus on the relative movement of the O ions. In c-BT, the local mode leading to the (tetragonal) instability polarized along x can then be expressed as $0.69 \hat{s}_{1x} + 0.73 \hat{s}_{2x}$, where \hat{s}_{1x} and \hat{s}_{2x} are the normalized symmetry modes depicted in Fig. 2.a. For a quantitative comparison to h-BT, we use the following approach: We calculate the projection of the total distortion of the TiO_6 groups in h-BT (as calculated from the ab-initio eigenvectors) into the polar modes transferred from the perovskite, so that we can measure the similarity between the soft modes of the two polymorphs [9].

h-BT	E_{2u} instability	TiO ₆ (1) distorted by	0.62/0.78
		TiO ₆ (2) distorted by	0.68/0.73
	A_{2u} soft mode	TiO ₆ (1) distorted by	0.67/0.70
		TiO ₆ (2) distorted by	0.63/0.74
c-BT	T_{1u} instability	TiO ₆ distorted by	0.69/0.73

TABLE 2. Distortions of the octahedra in h-BT corresponding to the E_{2u} instability and the A_{2u} soft mode. The distortions are given in the last column as s_1/s_2 . The data corresponding to the T_{1u} (irrep of $m3m$) ferroelectric instability of c-BT are included for comparison.

In order to transfer these \hat{s} to h-BT, we must consider the restrictions imposed by the symmetry of the soft modes. [For instance, a general A_{2u} distortion leads the crystal to a phase with $P6_3mc$ space group, in which the TiO₆(1) groups reduce their point symmetry to $3m$. As shown in Fig. 2.b, the combination of $\hat{s}_{i\alpha}$ modes leading to this symmetry breaking has the form (in components) $s_{ix} = s_{iy} = s_{iz}$ with $i = 1, 2$. Therefore, this is the pattern into which we project the total distortion of TiO₆(1) corresponding to the soft A_{2u} eigenvector.] Further details of the calculation can be found in Ref. [10]; the results are summarized in Table 2. We find that almost 100% of the structural change associated to both soft modes can be described in terms of c-BT type polar distortions (for the first row in Table 2 we have $(0.62^2 + 0.78^2) \times 100 = 99.3\%$) and, moreover, in all the cases the components s_1/s_2 are very similar in magnitude to those of the perovskite.

Thus, we conclude that the soft modes of the $P6_3/mmc$ phase of h-BT originate in the occurrence of chains of dipoles whose elementary constituents are of c-BT type. For the E_{2u} instability, the resulting $C222_1$ phase could be informally considered as *anti-ferroelectric* rather than as paraelectric, due to the appearance of chains of dipoles in the $x'y'$ layers that cancel one another. With respect to the A_{2u} soft mode, we confirm that it originates in the c-BT type (rhombohedral) distortion of the TiO₆ groups; this identification is further ratified by the calculation of the corresponding Born effective charge $Z^* = 11.29$, which is unusually large as in the perovskite ($Z^* = 9.956$) [11]. The calculation of the energy minima of the $C222_1$ and $P6_3mc$ (in this case, using the experimental unit cell in which the A_{2u} instability occurs) phases leads to significantly smaller distortions than those of c-BT, which indicates that the different stacking tends to inhibit the instabilities.

III OTHER OPTICAL LOW-ENERGY MODES.

In the previous section we have proved that the experimentally found soft modes of h-BT have the same microscopic origin as the instabilities of the perovskite; i.e., they stem from (two concrete distributions of) Ti \Rightarrow O–Ti \Rightarrow O type chains of dipoles. Now, it could be asked whether there are other zone-center soft modes

based on different distributions of this kind of chains. Particularly, there should be two (degenerate, transforming with E_{1u} irrep) ferroelectric soft modes involving polarization in the $x'y'$ plane, as well as other *anti-ferroelectric* modes. Nevertheless, we find that no more locally polar soft modes occur. In order to explain this result, let us remark that for the E_{2u} and A_{2u} soft modes, the distribution of Ti displacements is such that if one O ion is approached by one of its two Ti neighbors the second Ti ion moves away from it. We assume this is indicating the hybridization between Ti $3d$ and O $2p$ electronic states, which was shown to be essential for the occurrence of the c-BT ferroelectric instability by Cohen [12]. It can be checked that for any other zone-center distribution of dipoles in h-BT we always have that two Ti ions approach one O ion (for example, if the two Ti(2) ions in one of the $O_3-Ti-O_3-Ti-O_3$ groups depicted in Fig. 1 move in the same way in the $x'y'$ plane, there is at least one oxygen of the shared face that is approached by both) or that the second titanium does not move away from the oxygen. In the former case the effect of the hybridization is lost and the corresponding modes are hard (see the force-constant of the Ti dominated E_{1u} mode in Table 2); in the later case, the hardening effect is not so large, but the softness is lost. Thus, we conclude that the particular stacking of the TiO_6 groups in h-BT inhibits the existence of more soft modes due to this local “repulsive” effect [13].

In Table 1 we show the other (not experimentally reported) softest modes we have calculated from first-principles. All of them are composed of a distribution of rotations of the O_3 groups in the different $x'y'$ layers depicted in Fig. 1. In the case of A_{2g} , the rotations are coordinated so that the O_6 octahedra do not distort, and we have a Rigid Unit Mode. For B_{1u} and B_{2g} there exist a distortion of the octahedra, but the three modes are similar in that the effect of the volume change in their force-constants is very small compared to that of the locally polar modes. This *anomalous* behaviour has already been reported for RUMs [14], which usually present a negative Grüneisen parameter (the modes soften with the application of hydrostatic pressure); but the situation in h-BT is more complicated due to the marked anisotropy of the system. Work on the influence of the different strains of the hexagonal unit cell on these modes is in progress.

IV SUMMARY

We have presented a microscopic study of the two experimentally found soft modes of hexagonal barium titanate and proved that they originate in the occurrence of $Ti \Rightarrow O - Ti \Rightarrow O$ type chains of dipoles, just as the instabilities of the cubic perovskite, which is particularly striking in the case of the E_{2u} non-polar instability of the hexagonal phase. We have evidenced that the stacking of the TiO_6 groups is responsible for a local effect, related to the covalence enhancement between Ti and O ions, that inhibits the occurrence of other soft modes based on dipole chains. Finally, we have reported on the existence of soft RUMs (and near RUMs) in the structure.

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